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(54) **Method for producing gadolinium gallium garnet**

(57) There is disclosed a method for producing essentially iridium-free unicrystalline gadolinium gallium garnet from a melt of gadolinium and gallium oxides contained in an iridium crucible, which involves maintaining an atmosphere of nitrogen and about 0.5 to 3% oxygen in the crucible. The method reduces the number of iridium inclusions from the crucible in the finished crystal.

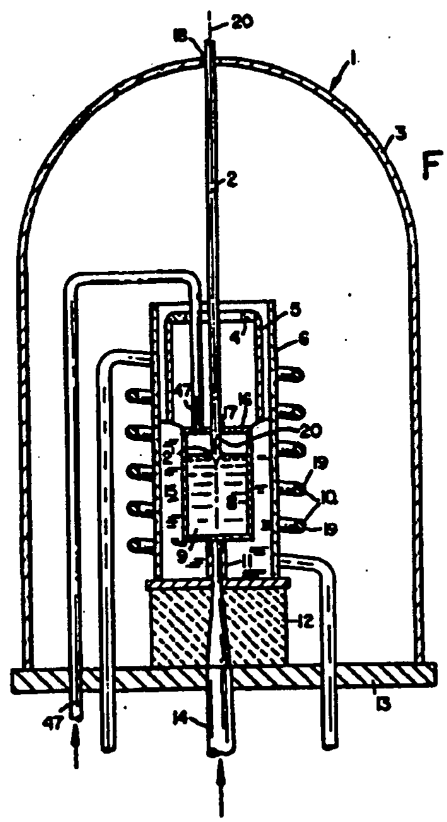

FIG. 1

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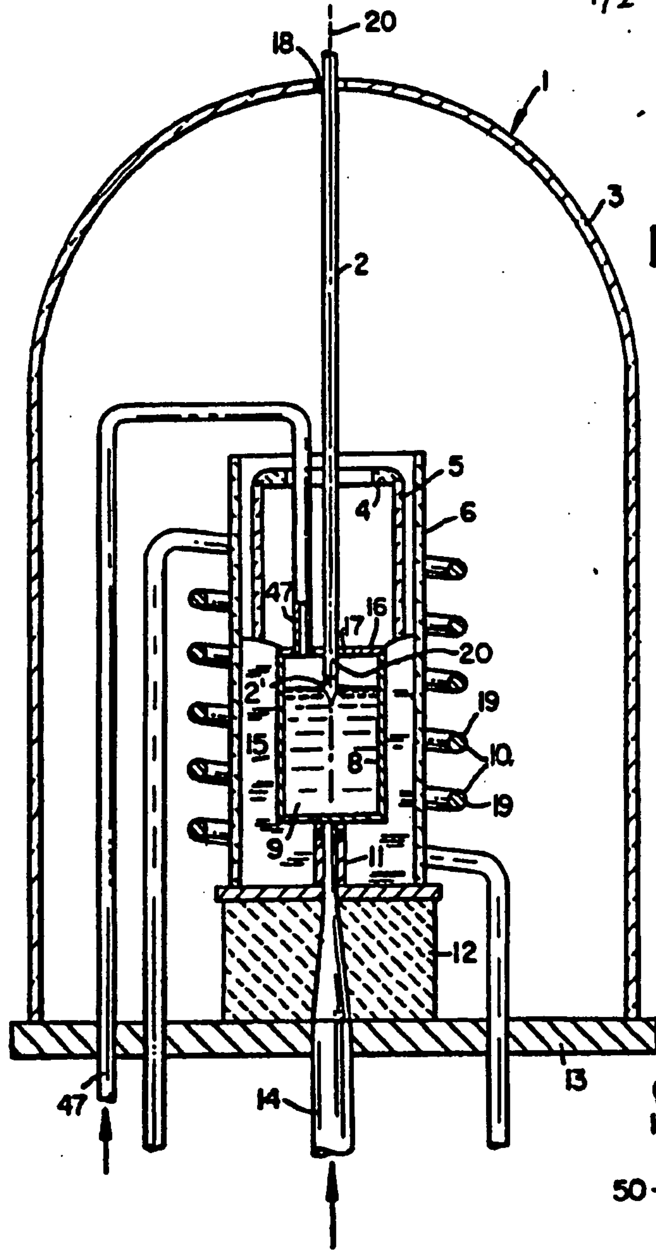

FIG. 1

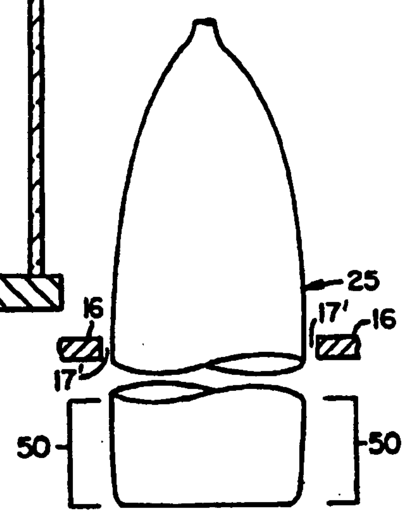

FIG. 2

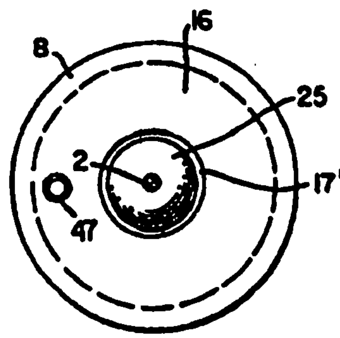

FIG. 3(c)

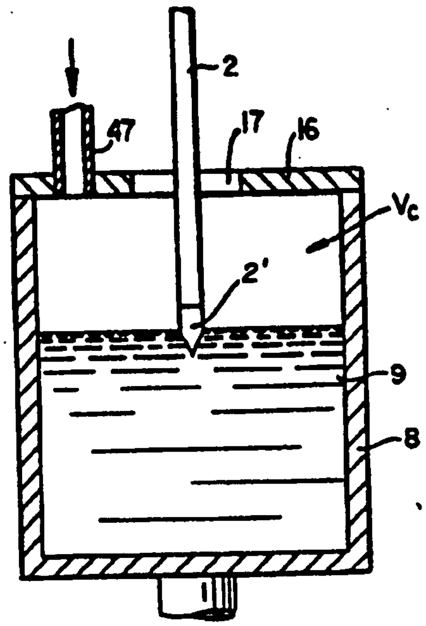

FIG. 3(a)

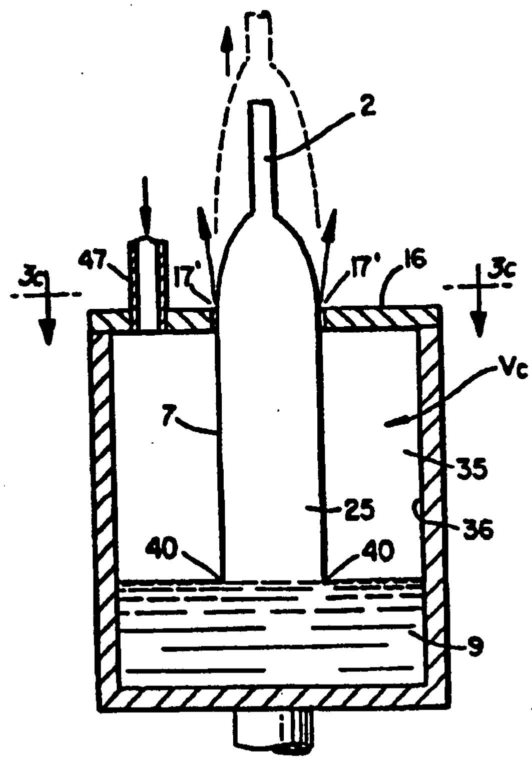

FIG. 3(b)

SPECIFICATION

Method for producing gadolinium gallium garnet

The present invention relates to a method for producing massive unicrystalline gadolinium gallium garnet material. More particularly, the present invention is directed to a method for producingsuch material from an oxide melt contained in an iridium crucible.

Unicrystalline gadolinium gallium garnet material in massive form is produced following the well known Czochralski technique by pulling a seed rod from a melt of Gd_2O_3 and Ga_2O_3 in a molar ratio of 3:5. The melt is most ususally contained in an iridium crucible, iridium being considered the most desirable metal for this purpose on account of its known physical and chemical properties. Also, it is known to provide a cover member or lid formed of iridium for the iridium crucible which acts as a radiation heat shield. The gadolinium gallium garnet is produced in the form of an elongate boule of circular cross-section which is subsequently sawed into wafers for use as substrates in electronic applications such as the epitaxial growth of iron garnet film. It is very important that these substrates, and hence the crystal from which they are formed, be free of impurities, e.g. iridium inclusions. This is so since such inclusions will propagate into epitaxial layers formed on crystalline substrates with well known detrimental effects.

It has been found that the above-noted iridium inclusions occur with significant frequency in the lower section of Czochralski grown boules, i.e. in the last grown section of the boule.

The method of the present invention for producing unicrystalline gadolinium gallium garnet boules of substantially circular cross-section involves the following steps:

(i) forming a melt by heating a mixture of Gd_2O_3 and Ga_2O_3 in a molar ratio of 3:5 in an iridium crucible having an iridium cover member with a circular opening positioned above the surface of the melt only slightly larger than the cross-section of the bule to be produced the melt being at a temperature in the range of 1700 to 1800°C.

(ii) Inserting a seed rod of unicrystalline gadolinium gallium garnet through said circular opening in said iridium cover member into the melt,

(iii) providing n ambient atmosphere of nitrogen containing from about 0.5% to 3% oxygen by volume.

(iv) withdrawing the seed rod from the melt such that gadolinium gallium garnet material is solidified and crystallized on the seed rod to form a massive unicrystalline boule product of increasing length and having a substantially circular cross-section slightly less than the circular opening in said iridium cover member, said boule passing through said circular opening in said iridium cover member as the length of said boule increases to substantially enclose the surface of the melt in said iridium crucible in a compartment defined by the walls of said crucible, said iridium cover member and the adjacent side

(v) Introducing a continuous flow of nitrogen containing from about 0.5 to 3% by volume oxygen into said compartment at a rate sufficient to maintain an atmosphere in said compartment of nitrogen containing about 0.5 to 3% by volume oxygen.

The process of the present invention may result in massive unicrystalline gadolinium gallium garnet boules which are essentially free of iridium inclusions. The process of the invention may produce unicrystalline gasolinium gallium garnet boules which are virtually perfect.

The improvement of the present invention with respect to previous growth techniques using an iridium crucible and iridium cover member resides in the cotinuous maintenance of an atmosphere of nitrogen and about 0.5% to 3%, preferably 2% oxygen in the region within the crucible contiguous to the melt surface, crystal growth interface and the adjacently located bottom surface of the iridium cqver and the inner surface of the iridium crucible which is above the melt.

The invention will now be further described by reference to the accompanying drawings, in which:-

Figure 1 shows an apparatus suitable for the practice of the present invention and

Figure 2 illustrates a unicrystalline boule of substantially circular cross-section produced by the practice of the present invention.

Figure 3(a) shows the crucible arrangement of Figure 1 prior to the commencement of crystal growth and

Figures 3(b) and 3(c) show the arrangement of Figure 3(a) during crystal growth.

With reference to Figure 1, there is illustrated a chamber 1 for enclosing crystal pulling apparatus and the ambient gaseous atmosphere. Within chamber 1, a melt 9 of Gd_2O_3 and Ga_2O_3 in a molar ratio of 3:5 is contained in a crucible 8 which is fabricated from iridium. A cover member or lid 16, formed of iridium, having a central circular aperture 17 rests on top the crucible 8 and the lower surface thereof acts as a radiation shield in a manner known to the art to reduce heat loss from the melt 9. The central circular aperture 17 is designed to be only slightly larger in cross-section than the circular cross-section of the boule to be prodced, represented at 25 in Figure 2. The crucible 8 is bounded on its sides and bottom with insulation 15. The insulation is preferably zirconia and serves to: reduce the power required to sustain the melt 9; reduce thermal gradients along the crucible; and to dampen temperature fluctuations arising from line voltage fluctuations, convective cooling effects from the atmosphere, as well as other disturbances. Hollow tubing 11 forms an aperture through which the temperature of the bottom of the crucible 8 can be determined by, for example, a radiation pyrometer focused on the centre of the bottom of the crucible.

A ceramic washer 4, fabricated from alumina, for example, is supported by tubing 5 preferably of zirconia. The washer 4 serves as a secondary radiation shield and to restrict the convective currents of the atmosphere against entering the top of the crucible and reaching the growing crystal 7. Thus it

in the vicinity of the growing crystal and to augment the effects of the washer 16.

Sleeve 6, formed of silicon dioxide, for example, serves to contain the insulation 15 and serves as a part of the insulating assembly surrounding the crucible 8. The tubing 5 which serves to support the washer 4 also functions as a part of the insulating system.

The crucible 8 and its surrounding insulating assembly rests on a ceramic pedestal 12 composed of, for example, zirconium oxide (ZrO_2). The entire assembly is enclosed in a bell jar 3 sealed to a base plate 13. The base plate 13 is composed of any suitable material such as for example silicone-bonded fiber glass. The major portion of the ambient gas atmosphere intended for the inside of the bell jar 3, i.e. a gas atmosphere non-reactive with the melt in the crucible, e.g. nitrogen, with 0.5% to 3% preferably 2% by volume oxygen, is introduced in a continuous flow into sight tube 14 which communicates with tubing 11. The gas introduced into bell jar 3 exits through the hole 18 in the bell jar 3 through which the seed rod is inserted. Rod 2 e.g. made of Al_2O_3 has a seed portion 2' the form of unicrystalline gadolinium gallium garnet material having its longitudinal axis 20 common with the growth axis 30 of crystal 7 and the orientation of the unicrystalline material of seed 2' is a predetermined orientation depending on the ultimate industrial use. Such a seed rod can be routinely prepared and results in the production of a massive unicrystalline material.

Using the above-described apparatus, the temperature of the melt is maintained in the range of 1700° to 1800°C and a unicrystalline mass is pulled from the melt to provide a circular cross-section of increasing length, e.g. 6-18 inches and about 3 inches in diameter, following procedures known to the art as exemplified by U. S. patent 3,715,194. The resulting unicrystalline boule material represented at 25 in Figure 2 has a substantially circular uniform cross-section.

With reference to Figure 3(a), this view shows the iridium crucible 8, iridium lid 16, melt 9 and seed rod 7 shown in Figure 1 prior to crystal pulling. At such time, the gaseous atmosphere within the iridium crucible 8 above melt 9 is essentially the same as the desired ambient atmosphere in bell jar 1 which is introduced via tubing 11 of Figure 1. Figure 3(b) shows the arrangement of Figure 3(a) after crystal pulling has progressed and the length of the boule 25 being produced has increased so as to pass through aperture 17 of iridium lid 16. For this condition, which persists until the desired boule length is produced, e.g. 6 to 18 inches, a compartment 35 is formed which is defined by the lower surface of iridium lid 17, the inner wall 36 of iridium crucible 8 and the peripheral side of boule 25 and the melt surface. This compartment substantially encloses the surface of melt 9 therein and the ambient atmosphere in compartment 35 is the actual ambient atmosphere to which the melt 9, crystal growth interface 40 and the adjacent iridium surfaces are exposed. It has been discovered, as part of the present invention, that for the condition represented crystal pulling procedure, the ambient atmosphere in compartment 35, unless replenished, becomes increasingly depleted of oxygen relative to the ambient atmosphere in bell jar 3 since the only exposure to the desired ambient atmosphere in bell jar 3 is via the small opening 17' between the sides of boule 25 and lid 16 which does not permit complete replenishment or homogenization of the atmosphere in compartment 35. That is to say, the atmosphere in compartment 35 is essentially isolated from the ambient atmosphere of bell jar 3. The increasing depletion of oxygen in compartment 35 (unless replenished) and hence at the melt surface and the growth interface 40 leads to the increasing presence of iridium inclusions in the boule with the result that the last grown part of the boule, indicated at 50 in Figure 2, the growth interface of which was subjected to the most severe oxygen depletion effect, contains an undesirably large number of iridium inclusions, e.g. as much as 100/cm^3. The inclusions, as is known to the art, are discrete metallic platelets or particles 1-20 microns in diameter. In the present invention, this undesirable effect is avoided by introducing into compartment 35 a continuous flow of nitrogen containing from about 0.5 to 3%, preferably by 2% volume oxygen, e.g. by way of iridium tube 47 which is shown communicating with compartment 35 through the iridium cover member, or lid 16. The rate of gas flow through tube 47 into compartment 35 is such that the desired ambient gas atmosphere as in bell jar 3 is maintained in compartment 35 over the surface of the melt and at growth interface 40 throughout the crystal pulling procedure. As a result of this practice, the presence of undesirable iridium inclusions in the boule 25 is essentially avoided. The replenishing gas flow is, as shown in the drawing, preferably introduced through an aperture in iridium lid 16 which is located close to the side wall of the crucible so that the replenishing gas flow essentially continuously flushes compartment 35 to ensure the presence of the desired ambient pressure in compartment 35. Other arrangements for introducing replenishing flow into compartment 35 may be used, e.g. through the crucible side wall to achieve the same flushing effect.

A suitable rate of gas flow can be readily determined for the particular apparatus involved. For example, knowing the volume of the compartment 35, Vc, by measurement of calculation, for such volume, Vc, a suitable gas flow rate can be expressed as from 0.2 Vc to 15 Vc per minute. That is, if the volume of the compartment Vc is one cu. ft., a suitable gas flow range is from 0.2 to 15 cu. ft. per minute. Higher flow rates may possibly be used provided that the melt surface is not disturbed thereby. Since the compartment volume, Vc, necessarily increases as the melt lowers in the crucible during crystal growth this should be considers when selecting a gas flow rate.

Example I

About 11,500 grams of Gd_2O_3 and Ga_2O_3 in a molar ratio of 3:5 (3.02:4.98) were placed in an

inches, a wall thickness of 0.1 inch and a height of 5.75 inches. An iridium cover 5.5 inch diameter, 0.1 inch thick having a central circular aperture of 3.5 inch diameter was provided on top of the iridium crucible. The crucible was placed within an 8 turn induction heating coil having an I.D. of 7.5 inches. The crucible stood on a pedestal containing packed zirconia granules while the space between the coil and the crucible was also packed with zirconia granules. This entire apparatus was enclosed in an aluminum bell jar (28 cu. ft) having an aperture at its top. A nitrogen atmosphere containing about 2% by volume oxygen was provided inside the bell jar by means of an inlet located beneath the crucible and remote from the crucible. The gas flow was 40 cu. ft. per hour. An iridium tube (.25 inch I.D.) located 1 inch from the crucible side wall communicated with the interior of the crucible through the lid. For this Example there was no gas flow through the iridium tube. The induction heating coil was energized from a well known R.F. induction heating unit and the power was increased until the induced current in the iridium crucible heated it to a "white heat". Conductive heat from the iridium crucible formed a melt in the crucible. The height of the crucible wall above the melt at this time was about 0.5 inch. A unicrystalline gadolinium gallium garnet seed 0.375 inch diameter (<111> orientation) was lowered through the aperture in the iridium cover until it contacted the surface of the melt. The seed was then withdrawn from the melt at about 0.3 inch per hour for 30 hours. The height of the crucible wall above the melt when growth was terminated was 4.5 inches. A 9 inch long boule of 3.2 inch circular cross-section was obtained which contained numerous iridium inclusions (at least 100/cm^3) in the bottom, i.e. last formed 1/3 of the boule.

Example II

Essentially the same procedure as in Example I was followed except that nitrogen gas containing 2% oxygen by volume was caused to flow continuously through the iridium tube into the crucible at a rate of 10 cu. ft. per hour. A boule 3.2 inch in diameter and about 8 inches long was produced which had few iridium inclusions (not more than 5/cm^3) throughout its length.

Example III

Essentially the same procedure as in Example I was followed except that nitrogen gas containing 2% oxygen by volume was caused to flow continuously through the iridium tube into the crucible at a rate of 2 cu. ft. per hour. A boule 3.2 inch in diameter and about 8 inches long was produced which had few iridium inclusions (not more than 5/cm^3) throughout its length.

CLAIMS

1. A method for producing unicrystalline gadolinium gallium garnet boules of substantially circular cross-section by

(i) forming a melt by heating a mixture of Gd_2O-

crucible having an iridium cover member with a circular opening positioned above the surface of the melt only slightly larger than the cross-section of the boule to be produced,

(ii) inserting a seed rod of unicrystalline gadolinium gallium garnet through said circular opening in said iridium cover member into the melt,

(iii) providing an ambient atmosphere of nitrogen containing about 0.5 to 3% by volume oxygen surrounding said covered iridium crucible,

(iv) withdrawing the seed rod from the melt such that gadolinium gallium garnet material is solidified and crystallized on the seed rod to form a virtually perfect massive unicrystalline boule product of increasing length having a substantially circular cross-section which is only slightly less than the circular opening in said iridium cover member, said boule passing through said circular opening in said iridium cover member as the length of said boule increases to substantially enclose the surface of the melt in said iridium crucible in a compartment defined by the walls of said crucible, said iridium cover member, the peripheral side of said boule and the melt surface,

(v) introducing a continuous flow of nitrogen gas containing about 0.5 to 3% oxygen into said compartment at a rate sufficient to maintain about 0.5 to 3% by volume of oxygen in said compartment.

2. A method as claimed in claim 1 substantially as hereinbefore described in any one of the foregoing Examples.

3. A method as claimed in claim 1, substantially as hereinbefore described with reference to and as illustrated in any one of the accompanying drawings.

4. A unicrystalline gadolinium gallium garnet boule whenever produced by a process as claimed in any one of claims 1 to 3.

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